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Published:
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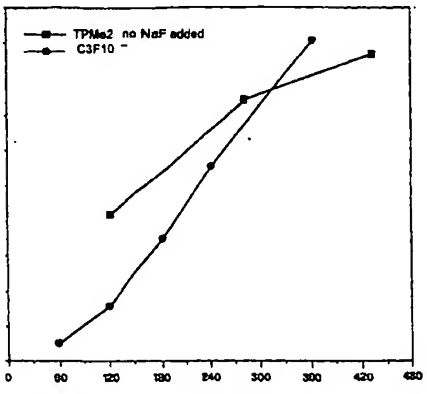
[Continued on next page]

(54) Title: AEROBIC CATALYSTS FOR ALCOHOL OXIDATION IN ORGANIC SOLVENTS AND IN SUPERCRITICAL CARBON DIOXIDE, PROCESS FOR THE PRODUCTION THEREOF AND THEIR USE IN OXIDATIVE CONVERSIONS



Aerobic benzyl alcohol oxidation to benzaldehyde in $scCO_2$ on TPAP trapped in C3-F-10 10% propyl-fluorinated silicium oxide matrices (rounded points) and 50% methylated TPAP-Me2 (square points)

(57) Abstract: Nanohybrid sol-gel materials, based on silica (ormosil) and doped with the ruthenium species tetra-*n*-propylammonium perruthenate (TPAP) are highly efficient catalysts for the selective oxidation of alcohols to carbonyls with oxygen at low pressure, in organic solvents as well as in carbon dioxide in supercritical state are decribed. Optimal conditions for the preparation and use thereof in liquid-phase as well as in supercritical CO2 were set by studying the structure-activity relationships of the materials, with particular reference to the surface hydrophobic/hydrophilic properties and to the textural ones.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB2004/052230

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J37/03 B01J23/46 C07C45/38 C07C45/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PAGLIARO M ET AL: "New recyclable catalysts for aerobic alcohols oxidation: sol-gel ormosils doped with TPAP" TETRAHEDRON LETTERS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 42, no. 27, 2 July 2001 (2001-07-02), pages 4511-4514, XP004245731 ISSN: 0040-4039 cited in the application the whole document ----- -/--	1-9, 13-25

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 June 2005	01.07.05

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB2004/052230

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BLELOCH, A. ET AL.: "Modified mesoporous silicate MCM-41 materials: immobilised perruthenate - a new highly active heterogenous oxidation catalyst for clean organic synthesis using molecular oxygen" CHEM. COMMUN., 1999, pages 1907-1908, XP002319966 cited in the application the whole document	1-9, 13-25
A	MARKO, I. ET AL.: "Efficient, aerobic, Ruthenium-catalyzed oxidation of alcohols into aldehydes and ketones" J.AM.CHEM.SOC., 1997, pages 12661-12662, XP002319967 the whole document	18, 21-23,25
A	STEELE, A.M. ET AL.: "Noble metal catalysed aerial oxidation of alcohols to aldehydes in supercritical carbon dioxide" CATALYSIS LETTERS, vol. 73, no. 1, 2001, pages 9-13, XP002319968 cited in the application page 12, paragraph 4 - page 13, paragraph 5; tables 1,2	18-20
X	CIRIMINNA ROSARIA ET AL: "Tailoring the Catalytic Performance of Sol-Gel-Encapsulated Tetra-n-propylammonium Perruthenate (TPAP) in Aerobic Oxidation of Alcohols" CHEM. EUR. J.; CHEMISTRY - A EUROPEAN JOURNAL OCT 17 2003, vol. 9, no. 20, 17 October 2003 (2003-10-17), pages 5067-5073, XP002330336 the whole document	10-14, 16,17, 21-25
P,X	CIRIMINNA, R. ET AL.: "The effect of material properties on the activity of sol-gel entrapped perruthenate under supercritical conditions" ADV. SYNTH. CATAL., 19 November 2003 (2003-11-19), pages 1261-1267, XP002330337 the whole document	10-15, 18-20, 23-25

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2004/052230

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-9, partially 13-25

A process for the production of nanohybrid sol-gel materials containing tetra-n-propylammonium perruthenate entrapped in the matrix according to claim 1 and their use as catalysts in the aerobic oxidation of alcohols.

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2. claims: 10-12, partially 13-25

A process for the production of nanohybrid sol-gel materials containing tetra-n-propylammonium perruthenate entrapped in the matrix according to claim 10 and their use as catalysts in the aerobic oxidation of alcohols.
